High-pressure Raman scattering and structural phase transition in YCrO$_4$

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The high-pressure structural properties of the zircon-type YCrO$_4$ with space group $I4_1/amd$ were investigated using Raman scattering techniques in a diamond anvil cell up to 28.9 GPa at room temperature. The abrupt changes in Raman spectra indicate that a pressure-induced structural phase transition occurs at a lower pressure 3.0 GPa, but a wide pressure region up to 15.1 GPa is needed to complete this phase transition. Moreover, the high-pressure phase can be quenched at ambient conditions. We calculated the mode Grüneisen parameters and assigned the new phase to be a scheelite-type structure in $I4_1/a$ symmetry based on the fact that the Raman spectrum of the new phase is similar to that of the scheelite-type YCrO$_4$ prepared at moderate pressure and temperature conditions. The effects of $3d^1$ electronic configuration on phase transition pressure and unusual Raman vibrations were discussed.

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I. INTRODUCTION

Zircon- and scheelite-type compounds with the chemical composition $ABX_4$ are kinds of attractive materials in theoretical studies as well as in applied realms related to solid-state scintillators, laser host materials, and optoelectronic devices.$^{1,5}$ The high-pressure structural properties of these materials have received renewed interest due to the significant advancements in integrated diamond anvil cell (DAC) techniques and synchrotron radiation as an available light source in experiments. It was shown that, at a moderate pressure, the tetragonal zircon-type compounds with space group $I4_1/amd$ ($Z=4$) would transform into another tetragonal scheelite phase. $^{6-13}$ In this structural phase transition process, coordination anions for $A$ and $B$ cations keep invariable, while the structural symmetry will decline into $I4_1/a$ ($Z=4$). In addition, experiments indicated that the tetragonal scheelite-type phase also is unstable under high pressure. When pressure further increases, it usually evolves toward a more compacted monoclinic structure concomitant with the increase of coordination number of the $B$-site cation. $^{14-22}$ Detailed descriptions on the interesting high-pressure structural behaviors of the scheelite-type compounds were reported in Ref. 22.

YCrO$_4$ crystallizes into a tetragonal zircon-type lattice at ambient conditions. $^{23}$ It consists of the edge-sharing CrO$_4$ and YO$_8$ structural units. Along $a$-axis direction, the larger YO$_8$ dodecahedra directly connect each other, while they alternately link with the compacted CrO$_4$ tetrahedra along $c$-axis direction. The constitution of YCrO$_4$ was described in more detail in Ref. 24. Due to the unusual out-shell electronic configuration ($3d^44s^6$) of Cr$^{5+}$ ion, magnetic properties were widely studied for YCrO$_4$ as well as for other isostructural $RCrO_4$ series materials.$^{25-29}$ where $R$ denotes rare earth elements except for La and Ce. However, no attention has been paid to the high-pressure structural behaviors of these compounds, even though the zircon-type structure is rather sensitive to pressure due to the less compacted constitution.

We present here the high-pressure Raman scattering investigations of YCrO$_4$ in order to explore pressure effects on crystal structure at room temperature. In addition, $d$- electronic contributions to phase transition pressure ($P_c$) and Raman vibrations were qualitatively studied.

II. EXPERIMENTAL

High pressure was generated using an improved Mao-Bell-type DAC with 500 $\mu$m culets up to 28.9 GPa in this experiment. The highly pure YCrO$_4$ polycrystalline powder synthesized using conventional solid-state reaction method$^{20}$ was carefully loaded into a 250 $\mu$m stainless-steel gasket hole. The mixture of 4:1 methanol-ethanol was used as pressure transmitting medium to obtain a hydrostatic pressure condition. Pressures were calibrated by ruby luminescence source. A 25$^\circ$ microscope objective lens was applied in order to focus the laser beam and collect the scattered light. The instrument resolution was 1 cm$^{-1}$. All the measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

A. Raman spectrum of YCrO$_4$ at ambient conditions

Figures 1(a) and 1(b) show some representative Raman spectra of YCrO$_4$ in the lower-frequency (100–650 cm$^{-1}$) and higher-frequency (700–1000 cm$^{-1}$) regions at different pressures, respectively. Group theory analysis$^{32}$ predicted that there are twelve Raman active phonon modes ($2A_{1g}$ $+4B_{1g}$ $+2B_{2g}$ $+5E_g$) for the zircon-type compounds in $I4_1/amd$ symmetry ($D_{4h}^{19}$). In our present experiment, eight Raman active phonon modes are discernable at ambient conditions. According to the assignment methods proposed by Jayaraman et al.,$^{33}$ six of them can be assigned as the internal vibration modes of CrO$_4$ tetrahedra: symmetric stretching $\nu_1$ ($A_g$), antisymmetric stretching $\nu_2$ ($A_g$ and $E_g$), symmetric bending $\nu_3$ ($A_g$ and $B_g$), antisymmetric bending $\nu_4$ ($B_g$); and
other two are assigned as the external translation modes of 
CrO$_4$ units: $T$ ($B_g$ and $E_g$). Furthermore, the stretching and 
bending modes reflect the vibrations of Cr-O and O-Cr-O 
bonds in CrO$_4$ tetrahedra, respectively. 

From the ambient-pressure Raman spectrum as shown in 
Fig. 1, it is known that the phonon frequencies of the stretching 
modes are higher than those of other modes. In addition, 
the intensity of $v_1$ ($A_g$) mode is the strongest and $v_2$ ($B_g$) the 
weakest. All of these are well in agreement with the general 
rule of Raman modes of the zircon-type compounds as re-
ported in Ref. 34. However, when compared with many other 
isostructural compounds such as CaCrO$_4$ and RV$_4$ ($R$=Y, Dy, and Tb), there is a large increase in the phonon 
frequency of $v_4$ ($B_g$) mode in YCrO$_4$. This is related to the 
effects of 3$d^1$ electronic interactions of Cr$^{5+}$ ions as dis-
cussed later.

B. Pressure-related Raman spectra

As presented in Fig. 1, the Raman active modes of the 
zircon-type YCrO$_4$ are rather sensitive to pressure. Just when 
pressure reaches 3.0 GPa, all the lower-frequency Raman 
peaks, as well as the $v_3$ ($E_g$) peak have disappeared. In ad-
dition, seven new Raman peaks (sign with $\omega_1$, $\omega_2$, $\omega_3$, $\omega_5$, $\omega_7$, $\omega_8$, and $\omega_9$, respectively) are exhibited clearly. These are 
indicative of structural phase transition in YCrO$_4$. With pressure 
increasing to 5.6 GPa, two additional new Raman peaks ($\omega_4$ and $\omega_6$) also appear accompanying with the vanish of $v_3$ ($B_g$) mode. However, the intensity of $\omega_6$ and $\omega_7$ Raman 
peaks decline quickly with pressure due to the pressure-
induced broadened effect so that they cannot be identified up 
to 8.2 GPa. In addition, it is notable that the zircon-phase $v_1$ ($A_g$) vibrational mode always coexists with the new-phase 
Raman modes in a wider pressure region, and it just becomes 
ambiguous as pressure increases to 15.1 GPa. At this pres-
sure, the new-phase $\omega_4$ and $\omega_8$ Raman peaks also have be-
come indiscernible, and the $\omega_6$ and $\omega_7$ Raman peaks tend to 
overlap. Then with pressure up to 18.2 GPa, only the $\omega_9$ Raman peak is observable. To further explore whether there is other possible structural phase transition, pressure is pro-
moted to the highest 28.9 GPa. But only two large humps are 
observed in the whole phonon frequency region, as shown in 
Fig. 2. The sharp broadening of Raman peak probably results 
from pressure-driven structural disordering and/or the re-
duced hydrostatic pressure condition in DAC. But the ruby 
luminescence spectrum (see the inset in Fig. 2) shows the 
obvious separation and the fine symmetry for $R_1$ and $R_2$ 
peaks at 28.9 GPa. Therefore, structural disordering is the 
main cause for Raman peaks broadening under higher pres-
ture. As a matter of fact, pressure-induced structural disor-
dering or even amorphization is often observed.
Eventually, we gradually released pressure to the lowest 0.5 GPa, and only the new-phase Raman peaks were observed in the whole decompression process as shown in Fig. 3. Accordingly, it is concluded that the structural phase transition occurred at 3.0 GPa is nonreversible. The top pattern in Fig. 1 also presents the pressure-released Raman spectrum to 0.5 GPa in order to demonstrate the nonreversibility for this phase transition.

The pressure dependence of Raman phonon frequencies in the compression process from 0 to 18.2 GPa is shown in Fig. 4. Linear least-square fittings were performed on these data as shown by the solid lines in the figure. The slopes of phonon frequency versus pressure, as well as the ambient-pressure frequencies are listed in Table I. These results are useful to calculate the mode Grüneisen parameters.

C. Zircon to scheelite phase transition in YCrO$_4$

1. Determination of the new phase

Pressure-related Raman spectra have shown that the structural phase transition is sluggish under high pressure in our experimental time scale (staying about 15 min at one pressure). Although this transition has occurred at a lower pressure 3.0 GPa, it will not complete until pressure reaches 15.1 GPa. In order to accelerate the structural transition, it probably is feasible to apply an appropriate temperature during compression. Most recently, we have successfully obtained a bulk YCrO$_4$ sample at moderate temperature and pressure ($P < 8$ GPa) (Ref. 24) conditions using a set of cubic anvil apparatus. This sample exhibits a different crystal structure from the zircon-type phase, just like the powder x-ray diffraction patterns shown in Fig. 5. Structural refinement results$^{24}$ reveal that it has a tetragonal scheelite-type crystal structure with space group $I4_1/a$. In particular, the scheelite-type YCrO$_4$ shows a similar Raman spectrum with that of the new phase of YCrO$_4$ observed in our Raman scattering experiment, as presented in Fig. 6. Therefore, we can reasonably conclude that the new phase occurred at 3.0 GPa also has a scheelite-type crystal structure in $I4_1/a$ symmetry ($C_{4h}^2$). Actually, a large number of available experimental data also support the fact that the zircon-type phase seemingly always transforms into a nonreversible scheelite phase at an appropriate pressure.$^{6-13}$

2. Mode Grüneisen parameters for both phases

Table I lists the ambient-pressure phonon frequencies $\omega_{0\text{i}}$, their pressure derivatives $\omega_{0\text{i}}/dP$ and mode Grüneisen parameters $\gamma_i$ for both phases of YCrO$_4$. It is known that the Cr-O bond stretching modes exhibit the larger Raman shift with pressure. In addition, the $\omega_i$ mode of the scheelite phase shows a negative pressure derivative. The mode Grüneisen parameters were calculated using the formula: $\gamma_i = (B_{0i}/\omega_{0i})(d\omega_i/dP)$, where $B_{0i}$ and $\omega_{0i}$ are the bulk modulus and the ambient-pressure phonon frequencies, respectively. The $d\omega_i/dP$ and the scheelite-phase $\omega_{0i}$ come from the linear fitting results as described above. Errandonea et al. have recently put forward an experiential criterion: $B_{0i}(\text{GPa}) = (610 \pm 110)Z_A/d_{A-O}^3$ to calculate the scheelite-phase bulk modulus,$^{22}$ where $Z_A$ is the formal charge for $A$-site cation.
Consequently, the bulk modulus of the scheelite-type YCrO$_4$ can be estimated to be 139 GPa. As far as YCrO$_4$ is concerned, the ambient-pressure phonon frequency of $v_1$ ($A_g$) vibrational mode declines from 863 cm$^{-1}$ to 804 cm$^{-1}$ as listed in Table I. According to the expression of force constant $\kappa = 1/2 \pi \nu/m$ ($\nu$ and $m$ denote phonon frequency and atomic renormalized mass, respectively), the Cr-O bond strength will decrease by about 3.5%. It implies that the Cr-O bond lengths in CrO$_4$ units will increase, and the density of the CrO$_4$ polyhedra probably will decline when phase transition happens. Therefore, we think that the increase of density in the zircon-scheelite transition in YCrO$_4$ does not directly result from the reduction of coordination polyhedra, but from their more efficient packing as well as the elimination of structural voids among polyhedra, just as Reid et al. reported on the prototype of the zircon ZrSiO$_4$.\cite{37}

3. Effects of 3d electrons on $P_c$ and Raman vibrations

Table II lists a series of physical parameters, such as phase transition pressure $P_c$, ionic radii,\cite{38} and so on for some

![FIG. 5.](image-url) (Color online) X-ray powder diffraction patterns and the corresponding indices for the zircon- and scheelite-type YCrO$_4$.

![FIG. 6.](image-url) (Color online) Raman spectra of (a) the pressure-released YCrO$_4$ to 0.5 GPa and (b) the scheelite-type YCrO$_4$ prepared using moderate temperature and pressure conditions.
TABLE II. Phase transition pressure \( P_c \) the radii of \( A \)-site cation and \( BO_4 \) units and their ratios, phonon frequencies of \( \nu_4 (B_g) \) mode for a series of \( ABO_4 \) zircon-type compounds.

<table>
<thead>
<tr>
<th>( ABO_4 ) type Compound</th>
<th>( P_c ) (GPa)</th>
<th>( R_A^a ) (Å)</th>
<th>( R_{BO_4}^a ) (Å)</th>
<th>( R_{BO_4}/R_A )</th>
<th>( \nu_4 (B_g) ) (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCrO(_4)</td>
<td>6.0</td>
<td>1.12</td>
<td>1.66</td>
<td>1.48</td>
<td>464</td>
<td>12</td>
</tr>
<tr>
<td>YCrO(_4)</td>
<td>3.0</td>
<td>1.019</td>
<td>1.745</td>
<td>1.712</td>
<td>552</td>
<td>this work</td>
</tr>
<tr>
<td>YVO(_4)</td>
<td>7.5/8.5</td>
<td>1.019</td>
<td>1.755</td>
<td>1.722</td>
<td>487</td>
<td>6 and 8</td>
</tr>
<tr>
<td>DyVO(_4)</td>
<td>6.5±0.3</td>
<td>1.027</td>
<td>1.755</td>
<td>1.709</td>
<td>482</td>
<td>7</td>
</tr>
<tr>
<td>TbVO(_4)</td>
<td>6.6±0.6</td>
<td>1.040</td>
<td>1.755</td>
<td>1.688</td>
<td>480</td>
<td>7</td>
</tr>
<tr>
<td>ZrSiO(_4)</td>
<td>19.7/23±1</td>
<td>0.84</td>
<td>1.66</td>
<td>1.98</td>
<td>—</td>
<td>11 and 10</td>
</tr>
</tbody>
</table>

\(^a\)Reference \(38\).

available data of \( ABO_4 \) zircon-type compounds at room temperature. Due to the smaller \( A \)-site cation radius as well as the more compacted \( BO_4 \) coordination polyhedra, the \( A^{4+}B^{4+}O_4 \)-type \( ZrSiO_4 \) displays the highest phase transition pressure. In addition, this type of compound usually has a larger bulk modulus, and potentially can be used as a kind of superhard materials.\(^{39}\) For \( A^{3+}B^{5+}O_4^- \) and \( A^{2+}B^{6+}O_4^- \)-type compounds, it was reported that \( P_c \) would increase with the increase of the ratio \( R_{BO_4}/R_A \), where \( R_{BO_4} \) and \( R_A \) present the radii of \( BO_4 \) units and \( A \)-site cation.\(^{41}\) \( R_{BO_4} \) were calculated according to the plus rule \( R_{BO_4}=R_B+R_O \) using Shannon’s ionic radii (\( R_O \) was set to be 1.40 Å).\(^{38}\) The values of \( R_A \), \( R_{BO_4} \) and \( R_{BO_4}/R_A \) for different compounds are shown in Table II. It is known that only YCrO\(_4\) deviates from the criterion mentioned above. Unlike other compounds listed in Table II with inert-element-like \( B \)-site cation configuration, there is a \( 3d^1 \) electron in the out shell of \( Cr^{3+} \) ion in YCrO\(_4\). During the compression, the cooperative interactions of these electrons will influence the system energy. As a result, the phase transition pressure of YCrO\(_4\) is no more consistent with the criterion. In our views, \( P_c \) is related to both ionic radius and electronic configuration in the zircon-type compounds. In addition, Raman scattering experiments showed that aside from the Cr-O bond stretching modes, the phonon frequencies of other modes usually do not exceed 500 cm\(^{-1}\) in \( ABO_4 \) zircon-type compounds as presented in Table II. However, YCrO\(_4\) exhibits unusual Raman vibrations. As a specific example, the frequency of the bending mode \( \nu_4 (B_g) \) reaches to 552 cm\(^{-1}\). We believe that the unusual Raman vibrations in YCrO\(_4\) also are related to the effects of \( 3d^1 \) electrons. The interactions of \( d \) electrons will influence the bond lengths and angles in \( CrO_4 \) polyhedra. Thereby it results in the unusual Raman behaviors of YCrO\(_4\).

IV. CONCLUSION

The high-pressure Raman scattering was performed on the zircon-type YCrO\(_4\) in 0–28.9 GPa at ambient temperature. The crystal structure of this compound sensitively depends on pressure. When pressure increases to 3.0 GPa, the tetragonal zircon phase will evolve toward a new phase. However this phase transition cannot complete until 15.1 GPa. The pressure-released Raman spectra show that the high-pressure new phase is quenchable to ambient conditions. Based on the similar Raman spectra, we assigned the new phase to be the same structure with our scheelite-type YCrO\(_4\) in \( H_4/\alpha \) symmetry prepared at moderate temperature and pressure conditions. The mode Grüneisen parameters were calculated according to the fitting results and the experiential criterion for bulk moduli. The cooperative interactions of \( d \) electrons in \( Cr^{3+} \) ions will influence the system energy and the bond lengths and angles of \( CrO_4 \) tetrahedra. These are responsible for the unusual \( P_c \) and Raman vibrations observed in YCrO\(_4\).

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